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(11) EP 0 953 624 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

03.11.1999 Bulletin 1999/44

(51) Int Cl.⁶: **C09K 11/06**, H05B 33/14, C07C 211/54

(21) Application number: 99303199.6

(22) Date of filing: 26.04.1999

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 28.04.1998 JP 13263698

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(54) Triarylamine compound and luminescent device

(57) A triarylamine compound used in a luminescent device is represented by the following general formula [1] or [2]:

wherein R¹ and R² are each independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryl group; Ar¹, Ar², Ar³, and Ar⁴ are each a substituted or unsubstituted aryl or heterocyclic group, which may be the same or different from each other; and at least one of Ar¹, Ar², Ar³, and Ar⁴ is a fused aromatic ring;

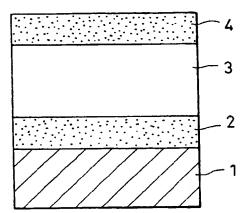
$$Ar^5$$
 Ar^6
 R^3
 R^4
 Ar^7
 Ar^8
 R^8

wherein R^3 and R^4 are each independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryl group; Ar^5 , Ar^6 , Ar^7 , and Ar^8 are each a substituted or unsubstituted aryl or heterocyclic group, which may be the same or different from each other; and at least one of Ar^5 , Ar^6 , Ar^7 , and Ar^8 is a π -conjugated aromatic hydrocarbon having 12 or more carbon atoms.

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The compound is used as a hole transport material or a luminescent material in the luminescent device.

FIG. I



Description

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BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a triarylamine compound and to a charge-injection-type luminescent device using the same. In particular, the present invention relates to a triarylamine compound applicable to a charge-injection-type luminescent device which directly converts injected charges into optical energy by an applied electric field, and relates to a luminescent device using the same.

Description of the Related Art

[0002] Pope et al., first discovered electroluminescence (EL) in an organic material, that is, single-crystal anthracene in 1963 (*J. Chem. Phys.*, <u>38</u>, 2042 (1963)). Subsequently, Helfinch and Schneider observed relatively strong EL in an injection EL material containing a solution system having a high injection efficiency in 1965 (*Phys. Rev. Lett.*, <u>14</u>, 229 (1965)).

[0003] Many studies of organic luminescent materials containing conjugated organic hosts and conjugated organic activators having condensed benzene rings have been disclosed in U.S. Patent Nos. 3,172,862, 3,173,050, and 3,710,167; *J. Chem. Phys.*, 44, 2902 (1966); *J. Chem. Phys.*, 58, 1542 (1973); and *Chem. Phys. Lett.*, 36, 345 (1975). Examples of disclosed organic hosts include naphthalene, anthracene, phenanthrene, tetracene, pyrene, benzpyrene, chrysene, picene, carbazole, fluorene, biphenyl, terphenyl, triphenylene oxide, dihalobiphenyl, trans-stilbene, and 1,4-diphenylbutadiene. Examples of disclosed activators include anthracene, tetracene and pentacene. Since these organic luminescent materials are provided as single layers having a thickness of more than 1 µm, a high electric field is required for luminescence. Under these circumferences, thin film devices formed by a vacuum deposition process have been proposed (for example, "Thin Solid Films" p. 94 (1982); *Polymer*, 24, 748 (1983); and *J. Appl. Phys.*, 25, L773 (1986)). Although the thin film devices are effective for reducing the driving voltage, their luminance is far from levels for practical use.

[0004] In recent years, Tang, et al., have developed an EL device having a high luminance at a low driving voltage (Appl. Phys. Lett., 51, 913 (1987) and U.S. Patent No. 4,356,429). The EL device is fabricated by depositing two significantly thin layers, that is, a charge transport layer and a luminescent layer, between the anode and the cathode by a vacuum deposition process. Such layered organic EL devices are disclosed in, for example, Japanese Patent Application Laid-Open Nos. 59-194393, 59-194393, 63-264692, and 3-163188, U.S. Patent Nos. 4,539,507 and 4,720,432, and Appl. Phys. Lett., 55, 1467 (1989).

[0005] Also, an EL device of a triple-layered structure having independently a carrier transport function and a luminescent ability was disclosed in *Jpn. J. Apply. Phys.*, <u>27</u>, L269 and L713 (1988). Since the carrier transportability is improved in such an EL device, the versatility of possible dyes in the luminescent layer is considerably increased. Further, the device configuration suggests feasibility of improved luminescence by effectively trapping holes and electrons (or excimers) in the central luminescent layer.

[0006] Layered organic EL devices are generally formed by vacuum deposition processes. EL devices having considerable luminance are also formed by casting processes (as described in, for example, Extended Abstracts (The 50th Autumn Meeting (1989), p. 1006 and The 51st Autumn Meeting (1990), p. 1041; The Japan Society of Applied Physics). Considerably high luminance is also achieved by a single-layered mixture-type EL device, in which the layer is formed by immersion-coating a solution containing polyvinyl carbazole as a hole transport compound, an oxadiazole derivative as an electron transport compound and coumarin-6 as a luminescent material, as described in Extended Abstracts of the 38th Spring Meeting 1991, p. 1086; The Japan Society of Applied Physics and Related Societies...

[0007] As described above, the organic EL devices have been significantly improved and have suggested the feasibility of a wide variety of applications; however, these EL devices have some problems in practical use, for example, insufficient luminance, changes in luminance during prolonged use, and deterioration by atmospheric gas containing oxygen and humidity. Further, the EL devices do not sufficiently satisfy needs for diverse wavelengths of luminescent light for precisely determining luminescent hues of blue, green and red colors in full-color displays, etc.

SUMMARY OF THE INVENTION

[0008] It is an object of the present invention to provide an organic compound applicable to a luminescent device having an optical output with significantly high efficiency and luminance.

[0009] It is another object of the present invention to provide an organic compound applicable to a luminescent device, which has diverse luminescent wavelengths, a variety of luminescent hues, and significantly high durability.

[0010] It is a further object of the present invention to provide a luminescent device easily produced at relatively low production cost and is highly safety.

[0011] An aspect of the present invention is a triarylamine compound represented by the following general formula [1]:

$$Ar^1$$
 N
 Ar^2
 Ar^3
 Ar^4
 Ar^4

wherein R^1 and R^2 are each independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryl group; Ar^1 , Ar^2 , Ar^3 , and Ar^4 are each a substituted or unsubstituted aryl or heterocyclic group, which may be the same or different from each other; and at least one of Ar^1 , Ar^2 , Ar^3 , and Ar^4 is a fused aromatic ring.

[0012] Another aspect of the present invention is a triarylamine compound represented by the following general formula [2]:

$$Ar^5$$
 Ar^6
 R^3
 R^4
 Ar^7
 Ar^8
 Ar^8

wherein R^3 and R^4 are each independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryl group; Ar^5 , Ar^6 , Ar^7 , and Ar^8 are each a substituted or unsubstituted aryl or heterocyclic group, which may be the same or different from each other; and at least one of Ar^5 , Ar^6 , Ar^7 , and Ar^8 is a π -conjugated aromatic hydrocarbon having 12 or more carbon atoms. [0013] A further aspect of the present invention is a luminescent device comprising a pair of electrodes, and at least one compound among the compounds represented by the general formulae [1] or [2] disposed therebetween. [0014] The organic luminescent device in accordance with the present invention is a thin lightweight solid device having a large area and high resolution and capable of high-speed operation, unlike conventional incandescent lamps,

fluorescent lamps, and inorganic luminescent diodes, and thus satisfies advanced requirements.

BRIEF DESCRIPTION OF THE DRAWINGS

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Fig. 1 is a cross-sectional view of an embodiment of a luminescent device in accordance with the present invention; Fig. 2 is a cross-sectional view of another embodiment of a luminescent device in accordance with the present invention;

Fig. 3 is a cross-sectional view of a further embodiment of a luminescent device in accordance with the present invention:

Fig. 4 is a cross-sectional view of a luminescent device in accordance with Example 7 of the present invention; and Fig. 5 is an infrared spectrum of an organic compound in accordance with the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0016] The present invention is characterized by a novel triarylamine compound represented by the general formula [1] or [2]:

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[0017] In the general formula [1], R^1 and R^2 are each independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryl group. [0018] Examples of alkyl groups include methyl, ethyl, n-propyl, and isopropyl groups; examples of alkoxy groups include methoxy, ethoxy, and phenoxy groups; and examples of aryl groups include phenyl, biphenyl, and naphthyl groups.

[0019] Examples of the substituent groups include halogen atoms, e.g., fluorine, chlorine, bromine, and iodine; alkyl groups, e.g., methyl, ethyl, n-proopyl, and iso-propyl groups; alkoxy groups, e.g., methoxy, ethoxy, and phenoxy groups; aralkyl groups, e.g., benzyl, phenetyl, and propylphenyl group; a nitro group; a cyano group; substituted amino groups, e.g., dimethyl amino, dibenzylamino, diphenylamino, and morpholino groups; aryl groups, e.g., phenyl, tolyl, biphenyl, naphthyl, anthryl, and pyrenyl groups; and heterocyclic groups, e.g., pyridyl, thienyl, furyl, quinolyl, and carbazolyl groups.

[0020] In the general formula [1], Ar¹, Ar², Ar³, and Ar⁴ are each a substituted or unsubstituted aryl or heterocyclic group, which may be the same or different from each other. Examples of the substituted or unsubstituted aryl groups include phenyl, biphenyl, terphenyl, naphthyl, anthryl, and fluorenyl. Examples of the substituted or unsubstituted heterocyclic groups include pyridyl, furyl, thienyl, and carbazolyl groups.

[0021] At least one of Ar1, Ar2, Ar3, and Ar4 is a fused aromatic ring. Examples of the fused aromatic rings include naphthyl, anthryl, acenaphthyl, phenanthryl, naphthathenyl, and fluoranthenyl rings. These fused aromatic rings may have substituent groups. Examples of the substituent groups include halogen atoms, e.g., fluorine, chlorine, bromine, and iodine; alkyl groups, e.g. methyl, ethyl, n-proopyl, and iso-propyl groups; alkoxy groups, e.g., methoxy, ethoxy, and phenoxy groups; aralkyl groups, e.g., benzyl, phenetyl, and propylphenyl group; a nitro group; acyano group; substituted amino groups, e.g., dimethyl amino, dibenzylamino, diphenylamino, and morpholino groups; aryl groups, e.g., phenyl, tolyl, biphenyl, naphthyl, anthryl, and pyrenyl groups; and heterocyclic groups, e.g., pyridyl, thienyl, furyl, quinolyl, and carbazolyl groups.

$$Ar^5$$
 Ar^6
 R^3
 R^4
 Ar^7
 Ar^8
[2]

[0022] In the general formula [2], R^3 and R^4 are the same as R^1 and R^2 , respectively, in the general formula [1], and R^5 , R^6 , R^7 , and R^8 are the same as R^1 , R^2 , R^3 , and R^4 , respectively, in the general formula [1]. At least one of R^5 , R^6 , R^7 , and R^8 is a π -conjugated aromatic hydrocarbon having 12 or more carbon atoms. Examples of the π -conjugated aromatic hydrocarbon having 12 or more carbon atoms include polyphenyls, i.e., biphenyl, p-terphenyl, and quaterphenyl; and stilbene derivatives, i.e., styryl and phenylstyryl.

[0023] The following are typical non-limiting examples of the compounds represented by the general formula [1] or [2].

[0024] Compounds represented by the general formula [1]

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5	Compound No.	\mathbb{R}^1	\mathbb{R}^2	Ar ¹	Ar ²
10	1	- H	- H	-0	
					. —
15			77		
20	2	- H	- H	-0	
25	3		- H		
30		– H			
<i>35</i>	4	4 - H - H	п		-8
40			- n	-0	

Compound	-1	~ ?	Ar ¹	Ar^2
No.	R ¹	R ² -	Ar ³	Ar ⁴
	- Н - Н		-000	
5		-н		
6	- H	- H -	- 0	
7	- H	Н – Н	-80	
			-	$\overline{}$
	- H		-0	
8		- CH ₃	-0	
				··· <u></u>

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Compound No.	R^1	R ²	Ar ¹	Ar ²
140.			——————————————————————————————————————	
9	- H	- н — 💮 -		
10	- H	- Br		-
		•		-(0)
11	- CH ₃	- CH ₃	-0	
	3		<u> </u>	
				-
12	- CH ₃	- CH ₃	-0	

	Compound	\mathbb{R}^1	${ m R}^2$	Ar ¹	Ar ²
5	No.			Ar ³	Ar ⁴
10	13	- CH	$-CH_3$		
	13	- CH ₃	- 0113	-0	-0
15 - - 20			-		
25	14	- CH ₃	- CH ₃		
20	15	- СН ₃	- CH ₃		√ N
30					√ N
35	16	16 - CH ₃			——CII3
40			- CI13	-0	$-$ CH $_3$

5	Compound No.	\mathbb{R}^1	R ²	Ar ¹	Ar ² Ar ⁴
10		- CH ₃	- CH ₃	-0	→CH ₃
	17				−CH ₃
15			077		-⟨CI
20	18	- CH ₃	- CH ₃	-0	- ⊘
25				-0	—— CH CH ₃
30	19	- CH ₃	- CH ₃	−CH ₃	
35				-0	-0
40	20	- CH ₃	- CH ₃	-0	-
					

5	Compound No.	\mathbb{R}^1	\mathbb{R}^2	Ar ¹	Ar ²
10			- CH ₃	-0	~ ○ ~ ○
15	21	- 0113			
	99	OH.	OH		-C ₂ H ₅
20	22	- CH ₃	- CH ₃		-C ₂ H ₅
25	00	O.I.	O.I.		-6-6
30	23	23 - CH ₃	- CH ₃		
35		O.T.	OTT.	$ \bigcirc$ CH ₃	NO ₂
40	24	24 - CH ₃	- CH ₃	$-$ CH $_3$	NO ₂

	_			\mathtt{Ar}^1	\mathbf{Ar}^2
	Compound No.	\mathbb{R}^1	R^2 —	Ar ³	Ar ⁴
-					
	25	- CH ₃	- CH ₃ -	CII ₃ —OCH ₃	-OCH ₃
	26	– $\mathrm{CH_3}$	- CH ₃ -	-0	
	27	- CH ₃	– CH ₃		
					—⟨○)— CH ₃
	28	- CH ₃	- CH ₃		$-$ CH $_3$

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Compound No.	R^1	R ²	Ar ¹	Ar ²
29	- CH ₃	- СН ₃		—(○)— CI
				—(CI
30	- СН ₃	- CH ₃		→
				-
31	$- \mathrm{C_2H_5}$	- C ₂ H ₅	-0	
			-0	
32	- C ₂ H ₅	– C ₂ H ₅		
			-0	-⊘-⊘

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Compound	R ¹	${ m R}^2$	Ar ¹	Ar ²
No.	10		Ar ³	Ar ⁴
	O II	O II	—————————————————————————————————————	$-$ CH $_3$
33	- C ₂ H ₅	- C ₂ H ₅	-CH ₃	$-$ CH 3
34	- C ₂ H ₅	- C ₂ H ₅		$-\!$
	- 225	-20 .	-0	-0
35	- C ₂ H ₅	- C ₂ H ₅		
	2 0			CH ₃
	- C ₃ H ₇	- C ₃ H ₇	-0	− CH 3
36				−CH ₃

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Compound No.	R ¹	\mathbb{R}^2	Ar ¹	Ar ² . Ar ⁴
	– C ₃ H ₇		——————————————————————————————————————	- -
37		- CH ₃	-8	
38	- C ₃ H ₇			→
		- 0)	-0	
		0.11		
39	− C ₄ H ₉	- C ₄ H ₉		→
40	- C ₄ H ₉	- C ₄ H ₉		
			-0	

	Compound	\mathbb{R}^1	\mathbf{p}^2	Ar ¹	Ar ²
5	No.	K*	ĸ	Ar ³	Ar ⁴
10	41	– C_4H_8			
	41	OCH ₃		-0	
15	40	0.11	C H		
20	42	- C ₈ H ₁₇	- C ₈ n ₁₇	-0	
25	40	0.11	O. II		-0
30	43	- C ₈ H ₁₇	- C ₈ H ₁₇		-0
<i>35</i>		Q II	0.11		— СН ₃
40	44	- C ₈ H ₁₇	- U ₈ П ₁₇		—⟨○) —СН ₃

Compound	\mathbb{R}^1	\mathbb{R}^2	Ar ¹	Ar^2
No.	I	16	Ar ³	. Ar ⁴
45	- C ₁₈ H ₃₇ - C ₁₈ H ₃	C II	-0	
45		- C ₁₈ H ₃₇	-0	

[0025] Compounds represented by the general formula [2]

25	Compound No.	\mathbb{R}^3	R ⁴	Ar ⁵ Ar ⁷	Ar ⁶ Ar ⁸
	40	- C ₂ H ₅	- C ₂ H ₅		—————————————————————————————————————
30	46				————CH ₃
35	45	C II	СП	$-\!$	$-\!$
	47	- C ₂ H ₅	- C ₂ H ₅	$-\!$	$-\!$
40	40	CH	O H	-CH = C	-
45	48	- C ₂ H ₅	- C ₂ H ₅	——————————————————————————————————————	

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C	ompound No.	R ³	R ⁴	Ar ⁵	Ar ⁶ Ar ⁸
				- \$-\$-\$	——————————————————————————————————————
	49	- C ₂ H ₅	- C ₂ H ₅	- \$-\$-\$	—————————————————————————————————————
	50	- C ₂ H ₅	- C ₂ H ₅		-O
	51	- C ₃ H ₇	- C ₃ H ₇		
				——————————————————————————————————————	\rightarrow CH = C
	52	- CH ₃	- C ₃ H ₇	——————————————————————————————————————	CH = C
-				—————————————————————————————————————	-О-О-СН3
53	53	$-C_3H_7$	$\rightarrow \bigcirc \rangle$		-О-О-сн₃
-					

5	Compound No.	\mathbb{R}^3	R ⁴	Ar ⁵	Ar ⁶
10			- C ₄ H ₉		$-\!$
15	54	- C ₄ n ₉			$-\!$
20		O.11	– C ₄ H ₉	-CH = C	_
25	55	− C ₄ H ₉		——————————————————————————————————————	
30	56	CH₃ —CH	−CH CH ₃	-	
,0		CH ₃		- ⊘ - ⊘	-
3 <i>5</i>	57	- C H	- C ₈ H ₁₇		$-$ CH $_3$
	<i></i>	- C ₈ H ₁₇		- ⊘ - ⊘	——————————————————————————————————————
40		0.77	- C ₈ H ₁₇	→	
15	58	– C ₈ H ₁₇			

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	Compound	\mathbb{R}^3	\mathbb{R}^4	Ar ⁵	Ar ⁶
5	No.			Ar ⁷	Ar ⁸
				-	- \$-\$
10	59	- C ₈ H ₁₇	- C ₈ H ₁₇	-	-
					$-\bigcirc-\bigcirc-\bigcirc$
15	60	– C ₁₈ H ₃₇	- C ₁₈ H ₃₇	- \$-\$-\$	-
	61	- CH ₃	- CH ₃	- (0) - (0)	-
20				-	
25		- CH ₃	- CH ₃		
30	62				
35					$-$ CH $_3$
40	63	- CH ₃	- CH ₃		→CH ₃
73					

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Compound No.	\mathbb{R}^3	\mathbb{R}^4	Ar ⁵	Ar ⁶
				—⟨○ > — CH ₃
64	- CH ₃	- CH ₃	-0-0	—(○)—CH ₃
			-O-O	(C)
65	- CH ₃	- CH ₃		—————————————————————————————————————
	2-22-2		- ⊘ - ⊘	$-\langle \hat{\mathbb{Q}} \rangle$
66	- CH ₃	- CH ₃	-	$-\langle \hat{p} \rangle$
	OII .		-{CH = CH -{C}}	
67	- CH ₃	- CH ₃	——————————————————————————————————————	-
	av.	O.I.	$-\bigcirc - CH = C$	→
68	- CH ₃	- CH ₃	——————————————————————————————————————	→ ◎

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-	Compound	\mathbb{R}^3	R ⁴	Ar ⁵	Ar ⁶
	No.	R-	K ·	Ar ⁷	Ar ⁸
-				-(CH = CH -(C)	——СН₃
	69	- CH ₃	- CH ₃	-(CH = CH -(C)	———— CH3
			- CH ₃	——————————————————————————————————————	
	70	- CH ₃		——————————————————————————————————————	- ⊘ - ⊘
				-CH = C O-O	→CH ₃
	71	- CH ₃	- CH ₃	-CH - C	— CH₃
				——————————————————————————————————————	——————————————————————————————————————
	72	- CH ₃	- CH ₃	——————————————————————————————————————	——————————————————————————————————————
				—————————————————————————————————————	-(0)
	73	- CH ₃	- CH ₃		-(0)
				· · · · · · · · · · · · · · · · · · ·	

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Compound No.	R^3	R ⁴	Ar ⁵	Ar ⁶
				$-\langle \langle \rangle \rangle$
74	- CH ₃	- CH ₃	-⊘-⊘	-√s>
75	- CH ₃	- CH ₃		
70	TT	TT		
76	– H	- H		
	T.T.	T.T.	-(C) - CH = CH -(C)	
77	- H	- H	-(CH = CH -(C)	
			——————————————————————————————————————	→
78	- H	- H	-CH = C	
			· · · · · · · · · · · · · · · · · · ·	

No.	R ³ - H	R ⁴ -	Ar ⁷ —⟨○⟩—⟨○⟩	Ar ⁸
	- H			$^{\text{CH}_3}$
	– H			- ⊘
79		- H -		−CH ₃
				$-\bigcirc$
80	- H	- H		
		-H -H	-	$-\langle \hat{Q} \rangle$
81	- H			$-\langle \tilde{0} \rangle$
				$-\bigcirc$
82	- H	- CH ₃		$-\bigcirc$
		- C ₃ H ₇		→
83	- H			
84	- H			$-\!$
			- 0-0	$\overline{-}$

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	Compound	R ³	R ⁴	Ar ⁵	Ar ⁶
	No.	K.	n ·	Ar ⁷	Ar ⁸
				- ⊘ - ⊘	-
	85	- H	- Br		- (-)-(-)
		- CTT	OV.		-(0)
	86	- CH ₃	- CH ₃		-(0)
		0.7.7	OV.	-⊘⊘	—CH ₃
	87	- CH ₃	- CH ₃		→CH ₃
			0.77		———— C1
1	88 .	- CH ₃	- CH ₃		— CI
		O.T.			
i	89	– CH ₃	- C ₃ H ₇	-	
1				$ \bigcirc$ $ \bigcirc$ $ C_2H_5$	$ \bigcirc$ $ \bigcirc$ $ \bigcirc$ $ -$
	90	- CH ₃	- C ₃ H ₇	$-\!$	-C ₂ H ₅

[0026] The luminescent device in accordance with the present invention has a layer or a plurality of layers composed of an organic compound disposed between an anode and a cathode, and at least one layer among the above organic layers contains a compound represented by the general formula [1] or [2].

[0027] The layer of the organic compound represented by the general formula [1] or [2] is formed between the anode and the cathode by a vacuum deposition process or a solution coating process. The thickness of the organic layer is preferably 2 μ m or less, and more preferably 0.5 μ m or less, and most preferably 0.05 to 0.5 μ m.

[0028] The present invention will now be described in further detail with reference to the drawings.

[0029] Fig. 1 is a schematic cross-sectional view of an embodiment of the luminescent device in accordance with the present invention. An anode 2, a luminescent layer 3 and a cathode 4 are formed on a substrate 1, in that order. In such a configuration, a usable luminescent layer 3 is generally composed of a single compound having hole trans-

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portability, electron transportability and luminescence, or a mixture of compounds each having one of these properties. **[0030]** Fig. 2 is a schematic cross-sectional view of another embodiment of the luminescent device in accordance with the present invention. An anode 2, a hole transport layer 5, an electron transport layer 6 and a cathode 4 are formed on a substrate 1, in that order. The hole transport layer 5 and the electron transport layer 6 function as a luminescent layer 3. In such a configuration, a usable hole transport layer 5 is generally composed of a luminescent material having hole transportability or a mixture including such a material and a non-luminescent material having hole transportability. The luminescent and non-luminescent materials may also have electron transportability or a mixture including such a material and a non-luminescent material having electron transportability or a mixture including such a material and a non-luminescent material having electron transportability. The luminescent and non-luminescent materials may also have hole transportability.

[0031] Fig. 3 is a schematic cross-sectional view of a further embodiment of the luminescent device in accordance with the present invention. An anode 2, a hole transport layer 5, a luminescent layer 3, an electron transport layer 6 and a cathode 4 are formed on a substrate 1 in that order. In this configuration, carrier transport and luminescence are performed in the individual layers. Such a configuration permits a wide variety of combinations of a material having excellent hole transportability, a material having excellent electron transportability and a material having excellent luminescence. Further, the configuration permits the use of various compounds emitting light at different wavelengths; hence the hue of the luminescent light can be controlled over a wide range. Effective trap of holes and electrons (or excimers) in the central luminescent layer will increase the luminescent efficiency.

[0032] Fig. 4 is a cross-sectional view of another luminescent device in accordance with the present invention. An anode 2, a hole injection-transport layer 7, a hole transport layer 5, an electron transport layer 6, and a cathode 4 are formed on a substrate 1, in that order. The hole injection-transport layer 7 facilitates hole injection from the anode 2. Thus, the luminescent device can maintain high efficiency for long driving times. In such a configuration, the hole transport layer 5 and/or the electron transport layer 6 function as a luminescent layer.

[0033] The compounds represented by the general formulae [1] and [2] have significantly superior luminescent characteristics to conventional compounds and can be used in all the electric field luminescent devices shown in Figs. 1 to 4. [0034] The compounds represented by the general formulae [1] and [2] have hole transportability and/or electron transportability depending on the structures thereof. In all the embodiments shown in Figs. 1 to 4, the compounds represented by the general formula [1] may be used alone or in combination, and the compounds represented by the general formula [2] may also be used alone or in combination. Alternatively, the compounds represented by the general formulae [1] and [2] may be used in combination.

[0035] As components of the luminescent layer in the luminescent device in accordance with the present invention, hole transport materials studied in the field of electrophotographic photosensitive members and known luminescent hole transport compounds as shown in Tables 1 to 5 or electron transport compounds and known luminescent electron transport materials as shown in Table 6 to 9 can be used with the compounds represented by the general formulae [1] and [2]. These compounds are used alone or in combination.

[0036] Table 10 illustrates examples of dopant dyes. The addition of a trace amount of dopant dye in the luminescent layer will significantly increase the luminescent efficiency or will change the luminescent color.

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Table 1 Hole Transport Compounds

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Table 2 Hole Transport Compounds

$$CH_3$$
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3

$$CH_3$$
 — $CH = CH$ — Cl

Table 3 Hole Transport Compounds

. 5 . O | C - O - (

$$= \begin{bmatrix} O & CH_3 & O \\ C & -O - \bigcirc -C & \bigcirc -CH_2CH_2 - \bigcirc \\ CH_3 & \bigcirc -OCO - CH_2CH_2 - \bigcirc \\ CH_3 & \bigcirc -OCO - CH_2CH_2O \end{bmatrix}_n$$

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Table 4 Hole Transport Compounds

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$$C_2H_5$$
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5

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$$CH = N - N$$

$$C_{2}H_{5}$$

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$$CH = N - N$$

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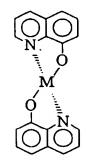
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Table 5 Hole Transport Compounds

$$\bigcirc N - \bigcirc N - \bigcirc N$$

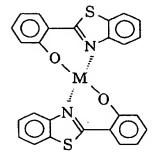
Table 6 Electron Transport Compounds

M: Al, Ga



M: Zn, Mg, Be

M: Zn, Mg, Be



M: Zn, Mg, Be

Table 7 Electron Transport Compounds

$$CH_3 - CH_3 N - N CH_3 CH_3$$

$$CH_3 - CH_3 - CH_3 - CH_3 - CH_3$$

$$CH_3 - CH_3 - CH_3$$

$$CH_3 - CH_3 - CH_3$$

$$O$$
 CH = CH O

Table 8 Electron Transport Compounds

$$\left(\begin{array}{c} 0\\ N\\ \end{array}\right)_{2}$$

` *35*

Table 9 Electron Transport Compounds

$$C = CH - CH = C$$

$$C = CH - CH = C$$

$$C = CH$$
 $CH = C$

$$\bigcirc -CH = CH - \bigcirc -CH = CH - \bigcirc -\bigcirc \bigcirc$$

$$C = CH - CH = C$$

Table 10 Dopant Dyes

CN CN CH_3 C_2H_5 C_2H_5 CH_3

[0037] In the luminescent device in accordance with the present invention, the luminescent layer containing the compounds represented by the general formulae [1] and [2] and the other organic layer are generally formed by a vacuum deposition process or using a binding resin.

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[0038] Non-limiting examples of the binding resins include polyvinyl carbazole resins, polycarbonate resins, polyester resins, polyarylate resins, butyral resins, polystyrene resins, polyvinyl acetal resins, diallyl phthalate resins, acrylic resins, methacrylic resins, phenol resins, epoxy resins, silicon resins, polysulfone resins, and urea resins. These binding resins can be used alone or in combination.

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[0039] Preferable anode materials have large work functions. Examples of such materials include nickel, gold, platinum, palladium, selenium, rhenium, and iridium; alloys thereof; and tin oxide, indium tin oxide, and copper iodide. Conductive polymers, such as poly(3-methylthiophene), polyphenylene sulfide and polypyrrole are also usable.

[0040] In contrast, preferable cathode materials have small work functions. Examples of such materials include silver, lead, tin, magnesium, aluminum, calcium, manganese, indium and chromium, and alloys thereof.

[0041] It is preferable that at least one electrode of the anode and cathode transmits 50% or more of incident light over the wavelength region of the luminescent light.

[0042] As the transparent substrate, glass and plastic films are used in the present invention.

10 [Examples]

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[0043] The present invention is described in further detail with reference to the following examples.

Synthesis of N,N,N',N'-tetra-(1-naphthyl)-2,7-diamino-9,9-dimethylfluorene (Compound 13)

[0044] Into a 100-ml egg-plant type flask, 2.24 g (10 mmol) of 2,7-diamino-9,9-dimethylfluorene, 15.22 g (160 mmol) of 1-iodonaphthalene, 6.91 g(50 mmol) of potassium carbonate, 12.71 g (200 mmol) of powdered copper, and 50 ml of o-dichlorobenzene were fed, and the mixture was refluxed with stirring for 24 hours.

[0045] The reactant solution was cooled and then filtered, and the filtrate was concentrated under reduced pressure. Into the concentrated solution, 35 ml of acetone was added and then filtered to collect precipitated crude crystal. The crude crystal was purified through a silica gel column using a toluene-hexane mixture, and 6.13 g (yield: 84.1%) of pale yellow fine crystal N,N,N',N'-tetra-(1-naphthyl)-2,7-diamino-9,9-dimethylfluorene (Compound 13) was prepared. [0046] The melting point (Tm) and the glass transition temperature (Tg) of the resulting compound were 331.0 to 332.7°C and 169°C, respectively, according to differential scanning calorimetry using Pyris 1 by Perkin Elmer Corporation. Fig. 5 is an IR spectrum of the compound by a KBr tablet method using an FT-IR spectrophotometer (FT-IR-420) by JASCO.

EXAMPLE 1

[0047] An indium tin oxide (ITO) film with a thickness of 100 nm was formed on a glass substrate by a sputtering process. After the transparent substrate was cleaned, a layer of Compound 12 with a thickness of 65 nm was deposited thereon at a deposition rate of 0.2 to 0.3 nm/sec, and then a Mg-Ag metallic electrode having an atomic ratio of Mg: Ag = 10:1 was formed by a vacuum deposition process at a deposition rate of 2.0 nm/sec under a vacuum pressure of 3 to 4×10-6 torr. A luminescent device was thereby formed.

[0048] A direct current of 10 V was applied between the ITO anode and the Mg-Ag cathode of the luminescent device. A current flow of 175 mA/cm² and a green luminescence with a luminance of 5,300 cd/m² were observed. A voltage with a current density of 3.0 mA/cm² was applied to the sample for 100 hours. The luminance was 160 cd/m² at the start and changed to 140 cd/m² at the end.

40 EXAMPLES 2 TO 6

[0049] Luminescent devices were prepared as in EXAMPLE 1 using Compounds 21, 36, 47, 72 and 88 instead of Compound 12. Table 11 shows the characteristics of these luminescent devices.

Table 11

EXAMPLE	Compound	In	itial	After 100 hours	
		Applied Voltage (V)	Luminance (cd/m²)	Applied Voltage (V)	Luminance (cd/m²)
2	21	5.3	350	5.9	345
3	36	6.7	275	7.8	280
4	47	4.8	345	5.7	330
5	72	4.9	550	5.5	530
6	88	5.7	450	3.8	450

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COMPARATIVE EXAMPLE 1

[0050] A luminescent device was prepared as in EXAMPLE 1 using the following compound instead of Compound 12.

$$CH_3$$
 N
 CH_3
 CH_3

[0051] A direct current of 15 V was applied between the ITO anode and the Mg-Ag cathode of the luminescent device. A current flow of 15 mA/cm² and a green luminescence with a luminance of 35 cd/m² were observed. A voltage with a current density of 27 mA/cm² was applied to the sample for 100 hours. The luminance was 100 cd/m² at the start and decreased to 8 cd/m² at the end.

[0052] The results of EXAMPLES 1 to 6 and COMPARATIVE EXAMPLE 1 show that the compounds in accordance with the present invention have high luminance and prolonged life compared to the comparative amine compound.

EXAMPLE 7

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[0053] A luminescent device shown in Fig. 4 was prepared as follows. An indium tin oxide (ITO) anode 2 with a thickness of 100 nm was formed on a glass substrate by a sputtering process. After the transparent substrate was cleaned, a m-MTDATA hole injection-transport layer 7 with a thickness of 20 nm was formed thereon, and a layer of Compound 32 with a thickness of 50 nm was deposited thereon as a hole transport layer 5. Furthermore, an electron transport layer of an electron transport compound (Alq₃) with a thickness of 65 nm was formed thereon, and then an aluminum cathode 4 with a thickness of 140 nm was formed thereon.

$$\begin{array}{c|c} & & & & \\ \hline \\ N & & & \\ \hline \\ N & & \\ \hline \\ CH_3 & & \\ CH_3 & & \\ \hline \\ CH_4 & & \\ \hline \\ CH_5 & & \\ CH_5 & & \\ \hline \\ CH_5 & & \\ CH_5 & & \\ \hline \\ CH_5 & & \\ CH_5 & & \\ \hline \\ CH_$$

$$Al_{II} \left(\begin{array}{c} O - \left(\begin{array}{c} \\ \\ \\ \end{array} \right) \\ Alq_3 \end{array} \right)_3$$

[0054] A direct current of 5 V was applied between the ITO anode and the aluminum cathode of the luminescent device. A current flow of 10 mA/cm² and a green luminescence with a luminance of 576 cd/m² were observed. A voltage

with a current density of 3.0 mA/cm² was applied to the sample for 100 hours. The luminance was 265 cd/m² at the start and slightly changed to 250 cd/m² at the end.

[0055] As described above, luminescent devices using compounds represented by the general formulae [1] and [2] in accordance with the present invention have significantly high luminance for a low applied-voltage, and high durability. A large device can be readily formed by a vacuum deposition process or a casting process with relatively low production costs.

[0056] While the present invention has been described with reference to what are presently considered to be the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. On the contrary, the invention is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims. The scope of the following claims is to be accorded the broadest interpretation so as to encompass all such modifications and equivalent structures and functions.

Claims

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1. A triarylamine compound represented by the following general formula [1]:

$$\begin{array}{c|c}
 & R^1 & R^2 \\
 & Ar^3 \\
 & Ar^4 & [1]
\end{array}$$

wherein R¹ and R² are each independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryl group; Ar¹, Ar², Ar³, and Ar⁴ are each a substituted or unsubstituted aryl or heterocyclic group, which may be the same or different from each other; and at least one of Ar¹, Ar², Ar³, and Ar⁴ is a fused aromatic ring.

- 2. A triarylamine compound according to claim 1, wherein at least one of Ar¹, Ar², Ar³, and Ar⁴ is selected from the group of a naphthyl group and an anthryl group.
- 3. A triarylamine compound represented by the following general formula [2]:

$$Ar^{5} N \longrightarrow Ar^{7}$$

$$Ar^{8} \qquad [2]$$

wherein R³ and R⁴ are each independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryl group; Ar⁵, Ar⁶, Ar⁷, and Ar⁶ are each a substituted or unsubstituted aryl or heterocyclic group, which may be the same or different from each other; and at least one of Ar⁶, Ar⁶, Ar⁷, and Ar⁶ is a π-conjugated aromatic hydrocarbon having 12 or more carbon atoms.

- 4. A triarylamine compound according to claim 3, wherein at least one of Ar⁵, Ar⁶, Ar⁷, and Ar⁸ is selected from the group of a polyphenyl group and a styryl group.
- 5. A luminescent device comprising a pair of electrodes and an organic compound layer disposed therebetween, the organic compound layer comprises a compound represented by the following general formula [1]:

wherein R¹ and R² are each independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryl group; Ar¹, Ar², Ar³, and Ar⁴ are each a substituted or unsubstituted aryl or heterocyclic group, which may be the same or different from each other; and at least one of Ar¹, Ar², Ar³, and Ar⁴ is a fused aromatic ring.

- 6. A luminescent device according to claim 5, wherein at least one of Ar¹, Ar², Ar³, and Ar⁴ is selected from the group of a naphthyl group and an anthryl group.
 - 7. A luminescent device according to claim 5, wherein the thickness of the organic compound layer is less than 2 µm.
- A luminescent device according to claim 7, wherein the thickness of the organic compound layer is in a range of 0.05 to 0.5 μm.
 - 9. A luminescent device according to claim 5, wherein the organic compound layer is used as a hole transport layer or a luminescent layer.
 - 10. A luminescent device comprising a pair of electrodes and an organic compound layer disposed therebetween, the organic compound layer comprises a compound represented by the following general formula [2]:

$$Ar^5$$
 Ar^6
 R^3
 R^4
 Ar^7
 Ar^8
 Ar^8

4.3

wherein R^3 and R^4 are each independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl. group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryl group; Ar^5 , Ar^6 , Ar^7 , and Ar^8 are each a substituted or unsubstituted aryl or heterocyclic group, which may be the same or different from each other; and at least one of Ar^5 , Ar^6 , Ar^7 , and Ar^8 is a π -conjugated aromatic hydrocarbon having 12 or more carbon atoms.

- 11. A luminescent device according to claim 10, wherein at least one of Ar⁵, Ar⁶, Ar⁷, and Ar⁸ is selected from the group of a polyphenyl group and a styryl group.
- 12. A luminescent device according to claim 10, wherein the thickness of the organic compound layer is less than $2\mu m$.
- 13. A luminescent device according to claim 12, wherein the thickness of the organic compound layer is in a range of 0.05 to 0.5 μm.
- 14. A luminescent device according to claim 10, wherein the organic compound layer is used as a hole transport layer or a luminescent layer.
- 55 15. A luminescent device comprising a pair of electrodes and an organic compound layer disposed-therebetween, the organic compound layer comprises a compound represented by the following general formula [1] and a compound represented by the following general formula [2]:

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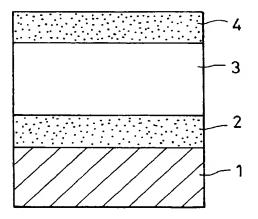
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wherein R¹ and R² are each independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryl group; Ar¹, Ar², Ar³, and Ar⁴ are each a substituted or unsubstituted aryl or heterocyclic group, which may be the same or different from each other; and at least one of Ar¹, Ar², Ar³, and Ar⁴ is a fused aromatic ring;

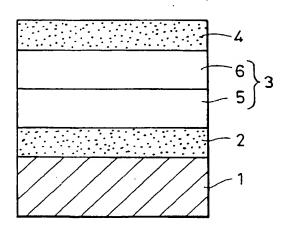
$$Ar^5$$
 Ar^6
 Ar^8
 R^3
 R^4
 Ar^7
 Ar^8

wherein R³ and R⁴ are each independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryl group; Ar⁵, Ar⁶, Ar⁷, and Ar⁶ are each a substituted or unsubstituted aryl or heterocyclic group, which may be the same or different from each other; and at least one of Ar⁶, Ar⁶, Ar⁷, and Ar⁶ is a π -conjugated aromatic hydrocarbon having 12 or more carbon atoms.

FIG. 1



F1G. 2



F1G. 3

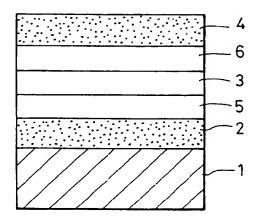
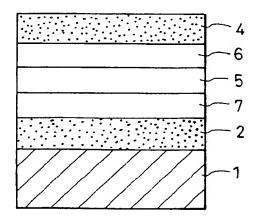
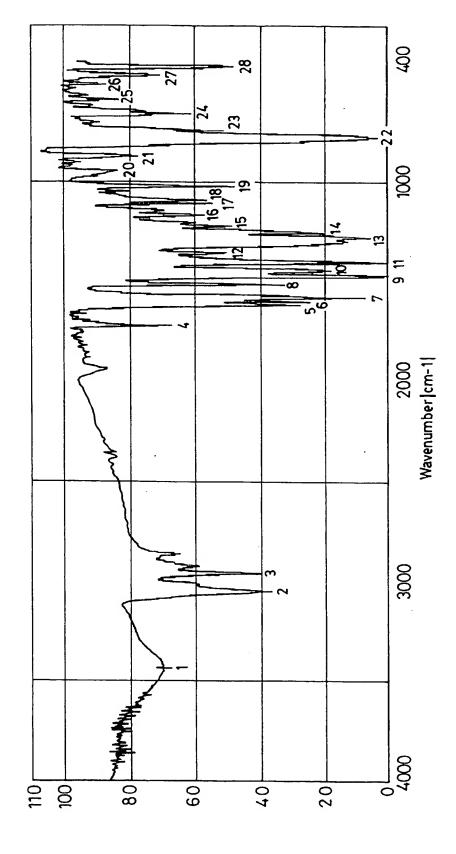


FIG. 4





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F1G. 5



EUROPEAN SEARCH REPORT

Application Number

EP 99 30 3199

Category	Citation of document with ind of relevant passage			Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	CHEMICAL ABSTRACTS, 29 June 1998 (1998-0 Columbus, Ohio, US; abstract no. 328604, NAKATSUKA, MASAKATSU electroluminescent d XP002110838 *Chemical Abstracts 206886-02-4, 206886- * abstract *	6-29) ET AL: "Organi evice" Registry Numbers 12-6, 206886-08-	c 0*	-15	C09K11/06 H05B33/14 C07C211/54
Х	& JP 10 095972 A (MI INC., JAPAN) 14 Apri	1 1998 (1998-04-	·14)	-15	
Ρ,Χ	EP 0 879 868 A (CANC 25 November 1998 (19 *compounds 13-24, 47	998-11-25)		-15	
X	PATENT ABSTRACTS OF vol. 018, no. 591 (0 11 November 1994 (19 & JP 06 220437 A (R) 01), 9 August 1994 (* abstract; examples	C-1272), 994-11-11) ICOH CO LTD;OTHEI (1994-08-09)	7 1	,3,5, -10, 2-15	TECHNICAL FIELDS SEARCHED (Int.CI.6) C09K H05B
X	PATENT ABSTRACTS OF vol. 098, no. 002, 30 January 1998 (199 & JF 09 268284 A (TO 14 October 1997 (199 * abstract; example	98-01-30) DYO INK MFG CO L 97-10-14)		3,4, 10-14	C07C
A	PATENT ABSTRACTS OF vol. 095, no. 005, 30 June 1995 (1995- & JP 07 053950 A (Told 28 February 1995 (1 * abstract; example	06-30) OYO INK MFG CO L 995-02-28)	TD),	1-15	
	The present search report has				
	Place of search	Date of completion of		6.	Examiner
	THE HAGUE	30 July 1	999 	Sr	nade, M
Y:p d A:te O:r	CATEGORY OF CITED DOCUMENTS anicularly relevant if taken alone anicularly relevant if combined with anol ocument of the same category achnological background ion-written disclosure itermediate document	E ea aft ther D. do L. do & : m	eory or principle riter patent docu- er the filing date cument cited in cument cited for ember of the sar current	the application of the control of th	ublished on, or on



EUROPEAN SEARCH REPORT

Application Number EP 99 30 3199

Category	Citation of document with indic		Relevant	CLASSIFICATION OF THE
A	of relevant passage PATENT ABSTRACTS OF J vol. 017, no. 309 (C- 14 June 1993 (1993-06 & JP 05 025473 A (MIT 2 February 1993 (1993 * abstract *	APAN 1070), -14) SUI TOATSU CHEM INC)	to claim	APPLICATION (Int.Cl.5)
D,A	US 4 720 432 A (VANSL 19 January 1988 (1988 * the whole document	-01-19)	1-15	
D,A	US 4 539 507 A (VANSL 3 September 1985 (198 * the whole document 	35-09-03)	1-15	
				TECHNICAL FIELDS SEARCHED (Int.Cl.6)
		·		
		·		
	The present search report has be	en drawn up for all claims		
	Place of search	Date of completion of the search		Examiner
	THE HAGUE	30 July 1999	Sha	ade, M
X:pa Y:pa doo A:led O:no	CATEGORY OF CITED DOCUMENTS ricularly relevant if taken alone ricularly relevant if combined with anothe cument of the same category chnological background in-written disclosure ermediate document	E : earlier patent after the filling r D : document cite L : document cite	ed in the application d for other reasons	lished on, or 1 3

45

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 99 30 3199

This armsx lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

30-07-1999

P 0622043 P 0926828 P 0705399 P 050254 S 472043	8 A 37 A 84 A 50 A	14-04-1998 25-11-1998 09-08-1994 14-10-1997 28-02-1995 02-02-1993 19-01-1988	NONE JP 11035532 A NONE NONE NONE NONE	09-02-1999
P 0622043 P 0926828 P 0705399 P 050254	37 A 84 A 50 A 73 A	09-08-1994 14-10-1997 28-02-1995 02-02-1993	NONE NONE NONE NONE	09-02-1999
P 0926828 P 0705399 P 050254	84 A 50 A 73 A	14-10-1997 28-02-1995 02-02-1993	NONE NONE NONE	
P 0705399	50 A 73 A	28-02-1995 02-02-1993	NONE NONE	
P 050254	73 A	02-02-1993	NONE	
S 472043	2 A	19-01-1988		
		., c	CA 1285638 A DE 3879727 A DE 3879727 T EP 0278758 A JP 2597377 B JP 63295695 A	06-05-199 21-10-199 17-08-198 02-04-199
35 453950)7 A	03-09-1985	CA 1213662 A DE 3471683 A EP 0120673 A JP 2037475 C JP 6032307 E JP 59194393 A	07-07-198 03-10-198 28-03-199 27-04-199

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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